

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS VI*. METALLOTROPIC REARRANGEMENT IN THE GROUP IVB CYCLO- PENTADIENYLS

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SUMMARY

The ^1H NMR spectra of the fluxional $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$ and $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ molecules have been studied at 100 MHz over a wide temperature range. The AA'BB'X spectrum has been analysed to show that the BB' signal ($\delta_A > \delta_B$) corresponds to the 1,4 protons. The metal in the cyclopentadienylgermane migrates through a 1,2 shift, as indicated by the unsymmetrical collapse of the olefin multiplets in such a way that a rapid broadening of the high-field side of the spectrum occurs. The AA'BB'X spectrum has been recorded for $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ at -150° but its complete analysis proved to be impossible. The thermodynamic characteristics of metallotropic migration in the Group IVB $\text{C}_5\text{H}_5\text{M}(\text{CH}_3)_3$ derivatives have been found. The free energy of activation for migration, ΔG_{300} , increases in the series Sn, Ge, Si, C. Essential features of the metallotropic rearrangement are discussed. The migration has been shown to proceed through a 1,2 shift in all cases (Si, Ge, Fe, Ru, H) where reliable data are available. An attempt is made to extend the concept of metallotropism to embrace both quasi-degenerate (indenyl) and non-degenerate (ring-substituted cyclopentadienyl) compounds.

A considerable amount of experimental evidence exists concerning the temperature dependence of the NMR spectra of the Group IVB cyclopentadienyls. In the silicon series, $\text{C}_5\text{H}_5\text{Si}(\text{CH}_3)_n\text{Cl}_{3-n}$, an intramolecular migration of silicon has been found¹, the migration proceeding predominantly via a 1,2 shift. The migration mechanism was essentially resolved through the assignment of the olefinic protons, which was only possible after the complicated NMR spectrum had been analysed in full detail including the signs of the coupling constants. Fritz and Kreiter² were the first to find a metallotropic rearrangement [that of $(\text{C}_5\text{H}_5)_2\text{Ge}(\text{CH}_3)_2$] revealed by the temperature dependence of the spectrum. Davison and Rakita³ observed a similar phenomenon for $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$. The spectrum of this compound, however, was obtained under slow exchange conditions (at -57°) and was not analysed in sufficient detail, so that the migration mechanism could not be unambiguously established. The fact that a metallotropic rearrangement does occur was proved in the case of (pentamethylcyclopentadienyl)trimethylgermane and, probably, (methylcyclopent-

* For Part V see ref. 1.

tadienyl)trimethylgermane $\text{CH}_3\text{C}_5\text{H}_4\text{Ge}(\text{CH}_3)_3$ ³. The rearrangement of $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$ was also proved through the use of ¹³C NMR spectroscopy⁴. Thermodynamic estimates of the migration in the germanium cyclopentadienyls were, unfortunately, never reported.

The situation is even more complicated if the tin derivatives are considered. At room temperature the compounds $(\text{C}_5\text{H}_5)_n\text{SnR}_{4-n}$ ($n=1, 2, 3, 4$; R is alkyl) display a singlet at δ_{H} equal to 5.8 to 5.9 ppm attributable to the five protons of the cyclopentadienyl ligand⁵ (an A_5 spectrum)*. The spectrum of $(\text{C}_5\text{H}_5)_4\text{Sn}$ is not affected by cooling the sample down² to -60° . By analogy with the properties of the Group IVB cyclopentadienyls it is reasonable to assume that the molecular structures of the tin derivatives are similar to those found for the derivatives of silicon⁷ or germanium⁸, in other words, they are σ -structures**.

These facts, *i.e.*, the A_5 -spectrum and the σ -structure, demonstrate unambiguously that the compound undergoes a rapid degenerate metallotropic rearrangement even at -60° . Davison and Rakita¹¹ attempted to slow down the rearrangement by cooling, but at -80° found nothing but a broadening of the signal; they could not record the slow exchange limiting spectrum and hence the mechanism remained unclear. The same difficulties were encountered in the study of $\text{C}_5(\text{CH}_3)_5\text{Sn}(\text{CH}_3)_3$ at -100° ¹¹.

Reliable metallotropic rearrangements have however been reported for the Group IVB indenyls (see, for example, refs. 12 and 13).

In this paper we wish to report PMR results obtained with the germanium or tin cyclopentadienyls over a wide temperature range. The difficulties mentioned above will be shown to be not insurmountable.

EXPERIMENTAL

PMR spectra were recorded on a Varian HA-100D spectrometer, the resolution being not worse than 0.5 Hz. Frequency sweep was used in all cases. The frequency of the second RF field (double resonance experiments) was adjusted by means of a D-890-B Muirhead audio frequency oscillator accurate to ± 0.1 Hz. The samples were 10% (v/v) solutions of $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$ or $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ in Freon, CF_2Cl_2 ***. This solvent was chosen in order to achieve as low an operating temperature as possible. Each of the samples contained a small addition of acetone which was employed as the standard for the internal lock system. Chemical shifts were converted to δ -scale [$\delta(\text{CH}_3\text{COCH}_3)$ 2.17 ppm]. Before recording the spectra each of the samples was twice distilled *in vacuo* in an argon atmosphere, degassed at 10^{-4} mm, and sealed.

The synthesis of the compound $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ is described in ref. 14.

The temperature dependences of the $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$ spectra are shown in Fig. 1. Similar spectra have been obtained earlier by Davison and Rakita³. At room tem-

* For the notation of the PMR spectra of the cyclopentadienyl compounds, see ref. 6.

** When this study was near completion, electronographic data appeared which proved unequivocally the σ -structure of $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ ⁹. In addition, indirect evidence in favour of the σ -structure of the tin derivatives has been supplied by the ¹³C spectra⁴ and ¹³C satellites in the PMR spectra¹⁰. NMR criteria for discerning between π - and σ -structures will be discussed in a forthcoming paper¹⁰. The σ -structure of $\text{C}_5\text{H}_5\text{M}(\text{CH}_3)_3$ (M is Ge, Sn) has been verified by IR spectroscopy³.

*** High temperature spectral measurements of $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$ were carried out using pure liquid samples.

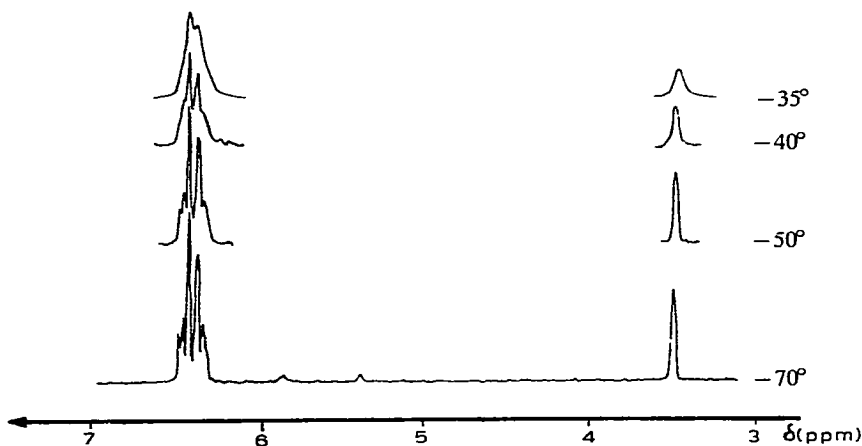


Fig. 1. PMR spectra of cyclopentadienyl protons in $C_5H_5Ge(CH_3)_3$ at various temperatures.

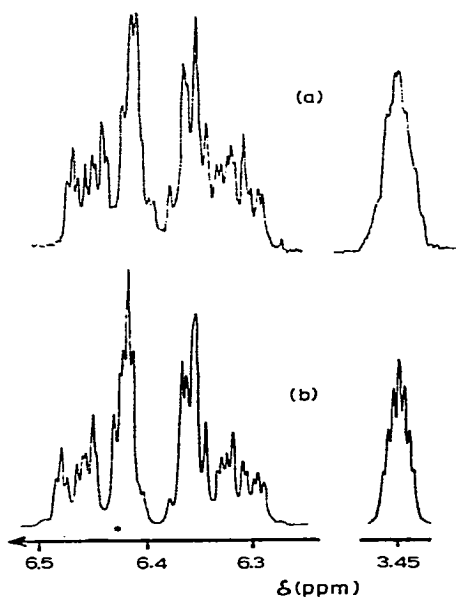


Fig. 2. Detailed fragments of PMR spectrum of $C_5H_5Ge(CH_3)_3$ at -70° . (a) experimental; (b) calculated with a YaMR-1 program.

perature the ring protons produce a broadened singlet which sharpens on heating. At -70° the five ring protons give a well-resolved AA'BB'X spectrum attributable to a nonfluxional* system (Fig. 2). In the intermediate temperature region (-40°), the AA'BB' part of the spectrum exhibits an unsymmetrical broadening, the BB' ($\delta_A > \delta_B$)

* Fluxional behaviour is defined, as a rule, with respect to the NMR time-scale. Thus, the use of the term "nonfluxional" implies that the dynamic process is not fast enough to yield observable NMR effects (i.e. rate constant $k \leq 1 \text{ sec}^{-1}$).

signals being broadened to a greater extent. According to Whitesides and Fleming¹⁵, this means that the metal migrates in $C_5H_5Ge(CH_3)_3$ intramolecularly, with one mechanism, either a 1,2 or 1,3 shift, predominating.

That a dynamic process takes place has been also been verified by saturation transfer experiments undertaken in the same manner as for silicon cyclopentadienyls^{1,6}.

The AA'BB'X spectrum has been analysed as for the spectra of silylated cyclopentadienes¹. The optimal coupling constants and chemical shifts are as follows: $\delta(A) = 6.44$, $\delta(B) = 6.33$, $\delta(X) = 3.45$ ppm; $J(AA') = J(BB') = +2.20$, $J(AB) = J(A'B') = +5.00$, $J(AB') = J(A'B) = +1.45$, $J(AX) = J(A'X) = 0.60$, $J(BX) = J(B'X) = 1.10$ Hz. The theoretical spectrum is independent of the signs of the constants $J(AX) = J(A'X)$ and $J(BX) = J(B'X)$. Tickling or INDOR¹ experiments are considerably hindered by the fact that the methyne signal is not sufficiently resolved (see Fig. 2). From the trends in the behaviour of the $J(HH)$ constants discussed extensively in ref.¹, it will be clear that any possibility, other than $J(AX) = J(A'X) = -0.60$ Hz and $J(BX) = J(B'X) = +1.10$ Hz, can be neglected*. Consequently, the upfield signal (BB', at 6.33 ppm) is a signal from the 1,4 protons and the migration proceeds predominantly through a 1,2 shift.

Cyclopentadienyltrimethyltin displays a broadening at -70° , similar to that observed in the spectra recorded by Davison and Rakita¹¹. At lower temperatures the broadening gradually increases leading to the AA'BB'X spectrum at -150° , this spectrum being that of a nonfluxional system (see Fig. 3)**. However, the shifts of the 1,4 and 2,3 protons are very close, and since operation at low temperatures (-100 to -150°) causes an additional broadening of all signals, due to inhomogeneity of the magnetic field, it was not possible to subject the spectrum to the type of analysis employed with $C_5H_5Si(CH_3)_3$ and $C_5H_5Ge(CH_3)_3$ ***. The spectrum of the ring protons in the nonfluxional compound $C_5H_5Sn(CH_3)_3$ consists of two signals at -150° , the ratio of integral intensities being 4/1. These signals have been assigned to the four olefin protons ($\delta_{1,2,3,4} = 6.51$ ppm) and to the methyne proton ($\delta_5 = 4.25$ ppm), and thus the shifts averaged by fast migration will be 6.05 ppm, *i.e.* very close to the observed value¹¹. The $^{117,119}Sn$ satellites have been found for the methyne proton signal and exhibit a spin-spin coupling constant $J(^{117,119}Sn-H_5)$ equal to 91 Hz. (A similar result has been obtained for the indenyl derivative of tin¹⁸.) Proton-tin spin-spin coupling is not exhibited by the other protons (1,2,3,4), but it is possible to estimate the coupling constants $J(^{117,119}Sn-H_{1,2,3,4})$, through the use of the relationship:

$$\langle J(Sn-H) \rangle = \frac{1}{5} [J(Sn-H_5) + 2J(Sn-H_1) + 2J(Sn-H_2)] \quad (1)$$

where $\langle J(Sn-H) \rangle$ is the value of the coupling constant $J(^{117,119}Sn-H)$ at the fast exchange limit. This value is equal to 22 Hz (21.8 and 22.9 Hz for ^{117}Sn and ^{119}Sn ,

* Indeed, $J_{15(45)}$ is always positive and close to 1.2 ± 0.1 Hz while $J_{25(35)}$ is usually negative and embraces a wide range, from -1.5 to 0.2 Hz^{1,16,17}.

** Similar results have been found quite recently by us for $C_5H_5Sn(C_2H_5)_3$. It is noteworthy that in this case the temperature T_c is equal to -165° , *i.e.* lower than that for $C_5H_5Sn(CH_3)_3$.

*** The coupling constants were tentatively analysed through the ^{13}C satellites in the PMR spectrum of $C_5H_5Sn(CH_3)_3$ ¹⁰, cf. also the discussion in ref. 1.

resp.). Thus two solutions are possible.

$$\begin{aligned} J(\text{Sn-H}_1) + J(\text{Sn-H}_2) &= -100 \text{ Hz} & \text{(a)} \\ J(\text{Sn-H}_1) + J(\text{Sn-H}_2) &= +10 \text{ Hz} & \text{(b)} \end{aligned}$$

Solution (a) corresponds to the case where the sign of the coupling constant $\langle J(\text{Sn-H}) \rangle$ is opposite to the sign of the coupling constant $J(\text{Sn-H}_5)$. This solution can be ruled out from the basis of known literature data¹³. The experimental data obtained in this study may be subjected to a similar analysis. Close examination of the experimental spectra obtained at the fast exchange limit (above collapse, at -80° to -100° , Fig. 3) shows that the following sequence exists in relation to the broadening of the signals: low-field satellite (lfs), central resonance (cr) and high-field satellite

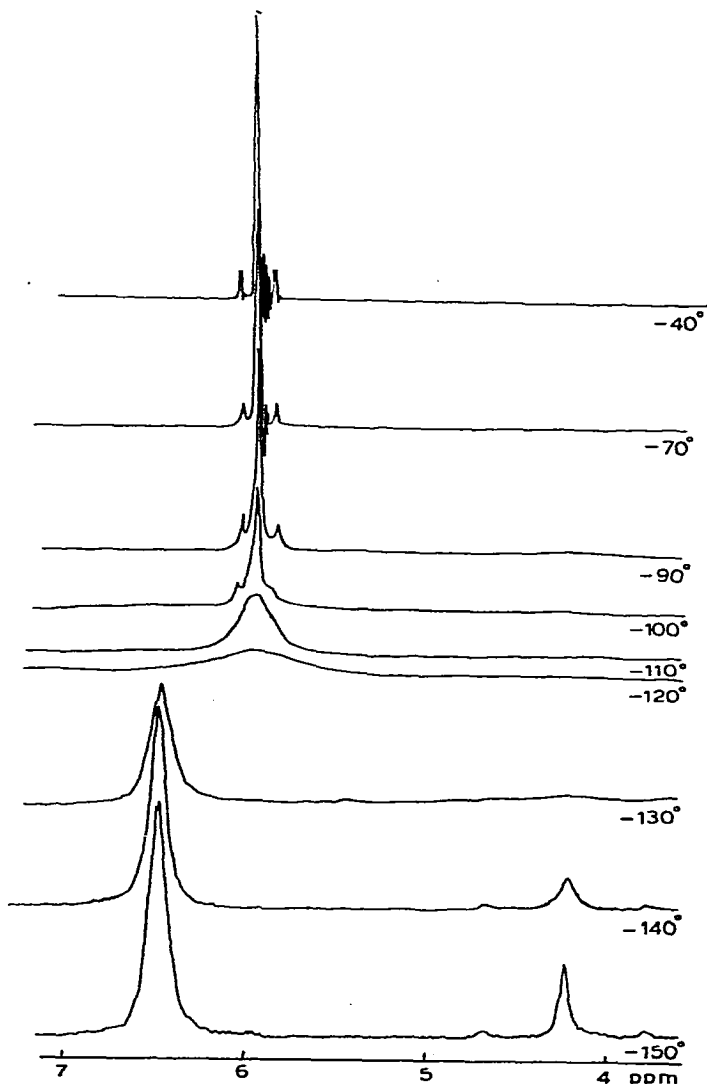


Fig. 3. PMR spectra of cyclopentadienyl protons in $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ at various temperatures.

TABLE I
INTRAMOLECULAR REARRANGEMENTS IN σ -CYCLOPENTADIENYL DERIVATIVES OF VARIOUS METALS

No.	Metal	Compound	Parameters			$\log A$	T_r^a (°C)	ΔG_{300}^b (kcal/mole)	Evidence ^c			Ref.
			E_a (kcal/mole)	$\Delta S_{300}^{\ddagger}$ (e.u.)	$\Delta G_{300}^{\ddagger}$ (kcal/mole)				d	e	f	
1	Si	$C_5H_5Si(CH_3)_3$	13.0 ± 1	-9.2 ± 4	11.3 ± 1	-23	15.2 ± 0.2	+	+	+	1	
2	Ge	$C_5H_5Ge(CH_3)_3$	9.2 ± 1	-15.8 ± 4	9.9 ± 1	-73	13.3 ± 1	+	+	+	This work	
3	Sn	$C_5H_5Sn(CH_3)_3$	7.8 ± 1	$+2 \pm 4$	13.8 ± 1	-152	6.6 ± 1	-	+	-	This work	
4	Fe	$C_5H_5Fe(CO)_2\pi-C_5H_5$	9.8 ± 0.1	-7.2 ± 0.5	11.7 ± 0.1	-92	11.3 ± 0.1	+	+	+	21	
			8.5 ± 0.8	-15.7 ± 3.5	9.8 ± 0.7	-86	12.6 ± 0.8	+	+	+	22	
5	Ru	$C_5H_5Ru(CO)_2\pi-C_5H_5$	10.3 ± 0.3	-14.0 ± 1.5	10.3 ± 0.3	-55	13.9 ± 0.3	+	+	+	21	
			9.6 ± 1.0	-15.3 ± 3.5	10.0 ± 0.7	-65	13.6 ± 1.0	+	+	+	22	
6	Hg	$(C_5H_5)_2Hg$				-140		-	+	-	24	
7	Cr	$C_5H_5Cr(NO)_2\pi-C_5H_5$				-110		+	+	-	25	
8	Mo	$C_5H_5Mo(NO)(\pi-C_5H_5)_2$				-52		-	-	-	26	
9	C	$5,5-(CH_3)_2C_5H_4$	43.3 ± 2.4	3 ± 3	14	$+347$	41.8	-	-	-	27	
10	H (D)	C_5H_6	24.3 ± 0.5	-5 ± 2.5	12.5	$+162$	2.2 ± 0.5	-	+	+	28 ^d	

^a T_r is temperature at which the migration rate, k , is equal to 1 sec^{-1} . For Si, Ge, Sn, Fe, Ru, C and H compounds T_r was found through use of the equation $k = A \cdot \exp[-E_a/(R \cdot T)]$, where $k = 1$; for other compounds approximate values are given on the basis of the data reported.^b For $C_5H_5Si(CH_3)_3$ see ref. 1. For other compounds the formula $\Delta G = E_a - R \cdot T - T \cdot \Delta S^{\ddagger}$ was used.^c The signs plus (+) and minus (-) mean that the evidence has, or has not, been reported here or elsewhere.^d Unsymmetrical broadening in NMR.^e Intramolecularity. ^f 1,2 Shift. ^g Ref. 28 deals with deuterium migration, so that the data in the Table are accurate to the isotopic effect. Our analysis^{2,9} shows that $\Delta G_{300(D)} - \Delta G_{300(H)} = 1 \text{ kcal/mole}$.

(hfs). At the fast exchange limit the line width $\Delta\nu_{\frac{1}{2}}$ is given by (see for example Ref. 1)

$$\Delta\nu_{\frac{1}{2}} = c \cdot \frac{(\Delta\nu)^2}{k} \quad (2)$$

where k is the rate constant of the exchange process, $\Delta\nu$ is the frequency difference between the resonances to be averaged and c is the proportionality constant which accounts for the probabilities of the states to be averaged. If solution (a) is true, the following values of $\Delta\nu$ may be deduced : 321 (lfs), 226 (cr), 131 (hfs), where the value of 226 Hz stands for the frequency difference between the AB and X parts of the spectrum. The value of $\Delta\nu$ for the satellites is found through the use of the relationship :

$$\Delta\nu_{\text{lfs}} = \Delta\nu_{\text{AB,X}} - \frac{1}{2}J(\text{Sn-H}_5) - \frac{1}{4}[J(\text{Sn-H}_1) + J(\text{Sn-H}_2)]$$

If the solution (b) is true, the values of $\Delta\nu$ should be equal to 186 (lfs), 226 (cr) and 266 (hfs) (Hz throughout). Solution (b) has been unambiguously verified experimentally (see Fig. 3)*.

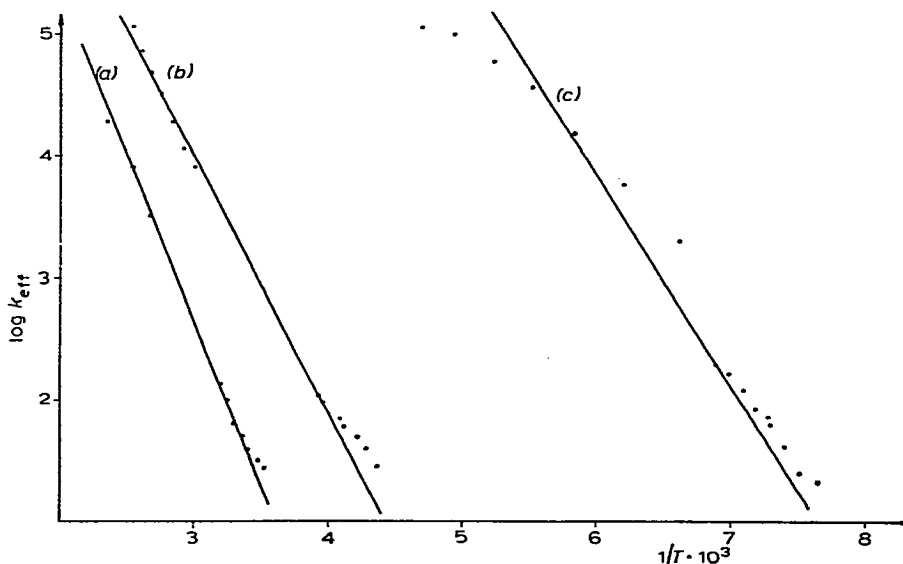


Fig. 4. $\log k_{\text{eff}}$ vs. $(1/T) \cdot 10^3$ for $\text{C}_5\text{H}_5\text{M}(\text{CH}_3)_3$ M being: (a) Si; (b) Ge; (c) Sn. k_{eff} is the effective value of the rate constant for the metallocyclic rearrangement.

In an attempt to estimate the thermodynamic characteristics of the metallocyclic rearrangement, $\text{C}_5\text{H}_5\text{Ge}(\text{CH}_3)_3$ and $\text{C}_5\text{H}_5\text{Sn}(\text{CH}_3)_3$ have been studied in a similar fashion to that employed for $\text{C}_5\text{H}_5\text{Si}(\text{CH}_3)_3$. Fig. 4 shows a plot of $\log k_{\text{eff}}$ vs. $1/T$. The quantity k_{eff} , which is the rate constant of the metallocyclic rearrangement, may be found from the line width at half-height under both slow and fast exchange conditions. Thermodynamic parameters for the process are listed in Table 1.

* Unsymmetrical broadening of the satellites has been demonstrated by West *et al.*²⁴ in a study of the PMR spectra of $\text{C}_5\text{H}_5\text{HgCl}$.

DISCUSSION

The PMR evidence above verifies that in the cyclopentadienyl derivatives of silicon¹ or germanium the metallotropic rearrangement proceeds predominantly via a 1,2 shift. The mechanism governing the shift is a central problem in the study of the fluxional molecules. Some workers¹⁹⁻²² have provided evidence in favour of a 1,2 shift in $\sigma\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-}\pi\text{-C}_5\text{H}_5$ and $\sigma\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2\text{-}\pi\text{-C}_5\text{H}_5$, and at present these systems are the only ones in which such an assignment has been made, and hence a migration mechanism selected, unambiguously. Thus, Cotton's assumption^{19,21,23} that a metal should always migrate via a 1,2 shift has been confirmed, since for all σ -cyclopentadienyl and σ -indenyl systems which have been studied this mechanism predominates. It is not clear now, however, whether a 1,3 shift can be completely ruled out.

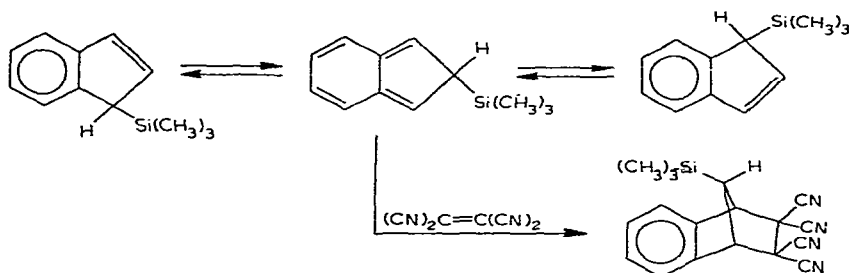
The existence of a metallotropic rearrangement has been demonstrated for many metal cyclopentadienyls (see Table 1). This Table also includes data on the migration of hydrogen (prototropic rearrangement) and carbon (methyl groups). The carbonotropic rearrangement in monosubstituted cyclopentadienes (*e.g.* in $\text{CH}_3\text{C}_5\text{H}_5$) is extremely difficult to observe because the compound undergoes a prototropic rearrangement which results in only the vinylic isomers of the isomeric cyclopentadienes appearing in the equilibrated mixture. The migratory ability of methyl groups, however, can be estimated roughly through the results obtained with polymethylated compounds (*e.g.* 5,5-dimethylcyclopentadiene²⁷). The migration of carbon was reported to occur at temperatures above 200° and to proceed via a 1,2-shift. The isostructural series of derivatives of the Group IVB elements (carbon included) reveals a pronounced regularity with an increase in the atomic number leading to a decrease in the free energy of activation, ΔG_{300} , and in T_r where T_r is the temperature at which the migration rate k is equal to 1 sec^{-1} , and where the system may be considered nonfluxional (for a more detailed discussion, see ref. 1). Hence, a metallotropic rearrangement may also be expected for lead derivatives, and at -170° it may be sufficiently slow with respect to the NMR time-scale*.

The σ -indenyl derivatives of Si, Ge, Sn and Hg have also been found to exhibit fluxional behaviour^{12,13,18,31,32}. Their rearrangements proceed via effective 1,3 metal shifts. Recently, however, Larrabee and Dowden¹² as well as Ashe³³ have argued that an alternative mode of migration could involve two successive 1,2 shifts. Despite the fact that the isoindene intermediate has a short lifetime, it can be trapped through the Diels-Alder reaction with *e.g.* tetracyanoethylene³³ as shown below**.

Metal migration is degenerate in the case of monosubstituted cyclopentadienyls, and the reader may remember that the term "fluxional molecule" was initially introduced to describe just such degenerate rearrangements³⁴. The properties of the indenyl systems, however, enable a natural extension to be made of the concept of fluxional behaviour. Indeed, the total 1,3 shift passes via a short-living isoindenyl

* NMR spectroscopy seems to be a less promising means of studying systems with such a high rate of migration. Methods involving lower characteristic times, such as IR spectroscopy or diffractonal analysis, may be more advantageous.

** The trimethylsilyl group of the adduct may be oriented in two ways. The structure shown here is based on an analogy with the structure of cyclopentadienyltrimethylsilane studied electronographically.



derivative A^* and therefore migration of metal in the indenyl derivative may be considered to be a quasi-degenerate process. The degeneration may be eliminated if low concentrations of the metastable moiety A^* may be detected. With indenyl derivatives, this may be done by using a Diels–Alder reaction specific to the isoindene structures of the type A^* . Furthermore, if we do not limit ourselves to a particular type of degeneration, non-degenerate processes may also be included. The resulting three types of rearrangements are summarized in Table 2.

This approach allows us, in principle, to compare parameters for the metal-lotropic rearrangement in monosubstituted cyclopentadienyl derivatives with the respective parameters obtained for indenyl systems (quasi-degenerate processes) and polymetallated or alkylated cyclopentadienes (non-degenerate processes).

In particular, when the parameters for the metal-lotropic rearrangements of Group IVB cyclopentadienyls (Table 1) and indenyls^{12,13} are compared, it can be seen, that for both the systems the activation energy increases in the series Sn, Ge, Si. This process proceeds in cyclopentadienyls with an activation energy which is on average 9 kcal/mole lower than that for the respective indenyls (this value is consistent with the energy difference between the indene and isoindene structures) and is accompanied by a decrease in entropy (ΔS^\ddagger) which may be as high as -15 e.u. Indenyl systems, as a rule, undergo migration at temperatures 150 to 180° higher than those for the corresponding cyclopentadienyl systems.

The fluxional behaviour of metal cyclopentadienyls substituted in the ring has been somewhat sparsely studied, *e.g.* pentamethylcyclopentadienyl derivatives of germanium or tin have been shown to undergo quite a normal metal-lotropic rearrangement^{3,11}. For di-substituted cyclopentadienes (*e.g.* for methylated cyclopentadienes), the process becomes non-degenerate, which makes its interpretation much more difficult. However, the spectra of $\text{CH}_3\text{C}_5\text{H}_4\text{Si}(\text{CH}_3)_3$ and $\text{CH}_3\text{C}_5\text{H}_4\text{Ge}(\text{CH}_3)_3$ have been analysed qualitatively^{3,11}, and indicate that the temperature interval at which the compounds became fluxional coincides with that characterising the respective monosubstituted compounds*.

When studying metal-lotropic (and prototropic^{28,36,37}) rearrangements, the intramolecular nature of the process should be proved and the rôle of the solvent clarified. Parallel intermolecular exchange processes have been found³¹ for mercury**.

* Cf. the data obtained for bis(pentamethylcyclopentadienyl)mercury³⁵, which is not subject to migration even at room temperatures, with that for $(\text{C}_5\text{H}_5)_2\text{Hg}^{2+}$ which becomes nonfluxional at temperatures as low as -140° . The results for $[\text{C}_5(\text{CH}_3)_5]_2\text{Hg}$ deserve careful scrutiny.

** Quite recently, intermolecular exchanges have been found with $\text{C}_5\text{H}_5\text{HgCH}_3$ and $\text{C}_5\text{H}_5\text{HgC}_2\text{H}_5$ by J. Lorberth. (J. Lorberth, private communication).

TABLE 2
REARRANGEMENT TYPES

Rearrangement type	Kinetical pattern	Potential energy curve	Example
Degenerate	$A \rightleftharpoons A^*$ $[A] \equiv [A^*]$		
Non-degenerate	$A \rightleftharpoons B$ $[A] \neq [B]$		
Quasi-degenerate	$A \rightleftharpoons A^* \rightleftharpoons A^{**}$ $[A] \equiv [A^{**}]$ $[A] \gg [A^*]$		

in the respective cyclopentadienyl compounds and for a prototropic rearrangement in solutions of methylcyclopentadiene³⁷. To prove the intramolecular nature of a migration, one must verify either satellites arising through the interaction of magnetic isotopes (Sn, Hg) with the C₅H₅ protons, or an unsymmetrical collapse in the olefinic domain (Si, Ge, Fe, Ru), or finally, the fact that the rate does not depend on either concentration or solvent. The migration may occur intermolecularly in strongly solvated systems.

If the solvent interacts with the substrate, the situation will be even more complicated³⁸. Thus the results obtained in a sulphur dioxide solvent, which forms insertion compounds with organometallics³⁹, have been found to be somewhat unclear^{15,40,41}.

The thermodynamic characteristics found in this study correlate well with the data calculated on the basis of an *a priori* model reported earlier by us^{42,43}. This model is being processed by a more accurate quantum-chemical method (CNDO/2), and it is hoped that the results will be published soon.

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